Influence of titanium dioxide nanoparticles on skin surface temperature at sunlight irradiation

I. Krasnikov,[1,*] A. Popov,[2,3] A. Seteikin,[1] and R. Myllylä[2]

[1]*Amur State University, 675027, Blagoveshchensk, Russia*
[2]*Optoelectronics and Measurement Techniques Laboratory, University of Oulu, 90014, Oulu, Finland*
[3]*International Laser Center, 119991, Moscow, Russia*
**ivkrasnikov@gmail.com*

Abstract: In this paper, we report about simulated distribution of density of absorbed light energy within human skin following light illumination with a combination of three wavelengths (310, 514 and 800 nm) with ratios similar to ultraviolet, visible and infrared fractions of the solar irradiance spectrum. We study heat distribution within the skin treated with a sunscreen containing TiO_2 nanoparticles. Our results show that administration of TiO_2 particles does not cause heat load on the tissue.

OCIS codes: (170.0170) Medical optics and biotechnology; (170.5280) Photon migration; (170.7050) Turbid media; (290.5850) Scattering, particles; (290.6815) Thermal emission

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1. Introduction

Skin protection against excessive doses of solar radiation causing skin cancer is a challenging task. Skin is a multilayered structure consisting of layers with specific physical properties [1]. Optical parameters of various skin layers such as absorption and scattering coefficient, refractive index and anisotropy of scattering, differ. The superficial skin layer (stratum corneum) serves as a natural protecting barrier for deeper-located layers containing living cells. From the optical point of view, its function is to prevent penetration of ultraviolet (UV) radiation into epidermis and dermis. In order to increase intrinsic protection of these layers by the upper-located stratum corneum, sunscreens containing chemical light-absorbing components were developed [2]. Currently, to achieve better UV protection, light-absorbing and scattering nanoparticles of zinc oxide (ZnO) or titanium dioxide (TiO_2) are used to partially replace chemical components in sunscreens [3].

A mathematical model developed by the authors in [4] was applied to the sunscreen-treated skin. It took into account the results of our earlier experiments for revealing localization of 100-nm TiO_2 nanoparticles within skin [5,6]. It was shown that even after multiple applications of nanoparticle-containing sunscreens, most of the particles remained localized superficially at a depth of 0-3 μm. In our previous papers [7–9], we also analyzed interaction between TiO_2 nanoparticles and stratum corneum in terms of absorption, reflectance and transmittance of UV light with the wavelengths of 310 and 400 nm. The focus was on the effect of size and concentration of TiO_2 nanoparticles for UV protection. We showed that nanoparticle-caused protection is mostly due to increased absorption of UV radiation. Energy of the absorbed light is released mainly in the form of heat, making consideration of heat load an important issue. It is worth noting, however, that as we observed in our experiments [10], UV-irradiated TiO_2 nanoparticles also produce free radicals and efficiency of this process depends on the particle size.

In the present paper, the wavelengths of 310, 514 and 800 nm were chosen as the representatives of the UV, visible and infrared (IR) spectral regions, respectively, in order to account for the whole solar spectrum. The aim of this paper is to show the effect of TiO_2 nanoparticles administration on heat load of skin in presence of solar light.

2. Materials and methods

In the model of skin with TiO_2 nanoparticles, the skin comprises three plain layers: stratum corneum, epidermis, and dermis (Fig. 1). The layers are situated horizontally and parallel to each other. Each layer owns specific physical parameters. The superficial layer of stratum corneum is homogeneously filled with TiO_2 particles with a volume fraction of 1-5%, corresponding to the experimental data and real concentration in sunscreens [4,6].

A developed code implementing the Monte Carlo method [11–13] was used for tracing photons inside the skin and for revealing distribution of absorbed light over depth.

Parameters of the skin layers with and without TiO_2 particles [1,14] required for our Monte Carlo simulations are presented in Table 1, where λ is light wavelength [nm], n is a refractive index, μ_a is an absorption coefficient [cm^{-1}], μ_s is a scattering coefficient [cm^{-1}], g is an anisotropy factor of light scattering and d is a layer thickness. Stratum corneum thickness is 20 μm, of which only the upper 3 μm contains TiO_2 particles (in Fig. 1 shown as a black stripe); epidermis thickness is 100 μm, and dermis 500 μm. The diameter of TiO_2 nanoparticles is 100 nm, as indicated in our previous experiments [5,6].

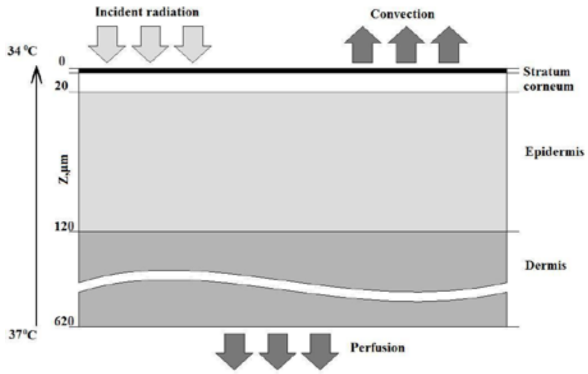

Fig. 1. Model of skin used in simulations.

Table 1. Optical parameters of skin layers[a,b]; percentage of particles in 3 μm sublayer in stratum corneum means volume fraction

Layer		λ, nm	n	μ_a, cm^{-1}	μ_s, cm^{-1}	g	d, μm
Stratum corneum	+1% TiO_2	310	1.5503	3000	4560	0.70	3
	+5% TiO_2		1.6315	12700	13200	0.55	1
	+1% TiO_2		1.5503	3000	4560	0.70	2[c]
	No TiO_2		1.53	600	2400	0.9	17
Epidermis			1.40	300	1400	0.71	100
Dermis			1.40	8.7	583	0.71	500
Stratum corneum	+1% TiO_2	514	1.5426	60	2200	0.70	3
	+5% TiO_2		1.593	60	4800	0.43	1
	+1% TiO_2		1.5426	60	2200	0.70	2[c]
	No TiO_2		1.53	60	1560	0.9	17
Epidermis			1.40	44	600	0.77	100
Dermis			1.40	2.2	250	0.77	500
Stratum corneum	+1% TiO_2	800	1.5408	3	500	0.76	3
	+5% TiO_2		1.584	3	840	0.49	1
	+1% TiO_2		1.5408	3	500	0.76	2[c]
	No TiO_2		1.53	3	420	0.9	17
Epidermis			1.40	40	420	0.85	100
Dermis			1.40	1.7	175	0.85	500

[a]Adapted from [1]
[b]Adapted from [14], page 1148.
[c]It means 1 μm of skin contains 5% of TiO_2, and 2 μm contains 1% of TiO_2, totaling 3 μm with TiO_2.

Optical parameters of TiO_2 particles, such as g-factor and scattering and absorption factors, were derived from TiO_2 and skin layer refractive indices [15], wavelengths of incident light and particle diameter, by means of the Mie theory implemented in the free software MieTab 7.23 [16]. The procedure is described in [6] in details.

In brief, the method is the following. The first part is the calculation of the distribution of light in skin and of the density of absorbed light power. To solve the problem, the Monte Carlo method is applied. The simulation process is based on the algorithm of photon tracing in a multi-layered medium described in [12]. The second part of the task is to calculate a temperature field in the skin. In order to obtain it, a non-stationary differential heat equation in the cylindrical coordinate system should be solved:

$$\rho c \frac{\partial T}{\partial t} = k\nabla^2 T + Q, \tag{1}$$

where k is a coefficient of thermal conductivity, T is temperature, Q is a heat source function, which was given by Monte-Carlo simulation as density of absorbed energy (the first part of the task), ρ is skin layer density, c is specific heat capacity, and t denotes time (see Table 2).

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Table 2. Thermo-physical properties of tissue layers[a]

Layer	k, W/(m·K)	ρ, kg/m^3	c, J/(kg·K)
Stratum corneum	0.266	1600	3700
Epidermis	0.498	1000	3200
Dermis	0.498	1000	3200

[a]Adapted from [19].

The solution is given by the finite-element methodology, using triangular finite elements of the first order; the mesh consists of about 4000 elements. Most of the elements are close to the surface for better approximation of the thin sublayer including nanoparticles. To get the solution in time domain, the Krank-Nicholson scheme is used [17,18].

As shown previously [19], for a healthy person a temperature about 37°C stabilizes at a 450- μm depth of skin. This is caused by thermal regulation produced by blood capillaries as internal heat transfer (perfusion) localized on the rear side of the modelled skin. In that case, we set the temperature equal to 37°C on the rear border of the skin model.

On the skin surface, where the heat exchange between the environment and the skin occurs, the following boundary condition is applied:

$$(k\frac{\partial T}{\partial z} - A(T - T_{ext})) = 0, \quad (2)$$

where A is a convective heat transfer coefficient, T_{ext} is temperature of the outer environment (usually it is taken equal to 20°C). This condition describes heat transfer on the surface of the stratum corneum (z = 0).

In the present paper, a 1-cm^2-large area of the skin surface is considered, with corresponding incident solar radiation power equal to 100 mW (integral over the wavelengths of 280-4000 nm); skin thickness is 620 μm. Such values are sufficient to reveal interaction between skin and light.

3. Results

Figure 2 represent heat load without and in presence of TiO_2 nanoparticles in stratum corneum. The particles are applied in the following way: 1% occupying 3-μm-thick superficial part of stratum corneum or 5% occupying 1 μm and 1% occupying 2 μm (totally 3 μm). Scattering and absorption coefficients of the part of stratum corneum where particles are present increase drastically, especially in the UV spectral range (Table 1).

Figure 3 depicts dynamics of the temperature on the surface of the stratum corneum and inside the skin with and without TiO_2 nanoparticles. As follows from the curves in Fig. 3(a), starting the 20th second after irradiation, the temperature stabilizes. The temperature in other layers (epidermis and dermis) increases (Fig. 3(b)) and stabilizes fast, in deep layers it remains at initial values, due to blood perfusion and convection.

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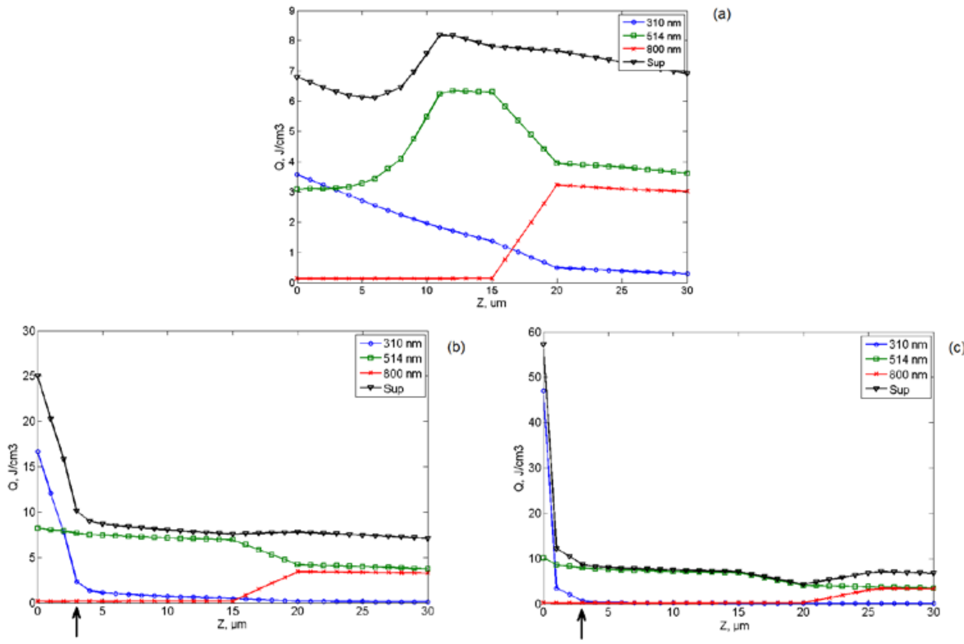

Fig. 2. Absorbed energy density over the skin depth, without particles (a), with 1% nanoparticles (b) and 5% nanoparticles (in 1 μm) + 1% nanoparticles (in 2 μm) (c). Individual components (310 nm – 5%, 514 nm – 50%, 800 nm – 45%) and their sum (denoted as "Sup"). Thickness of superficial layer containing nanoparticles is 3 μm. The arrow indicates the deepest location of particles.

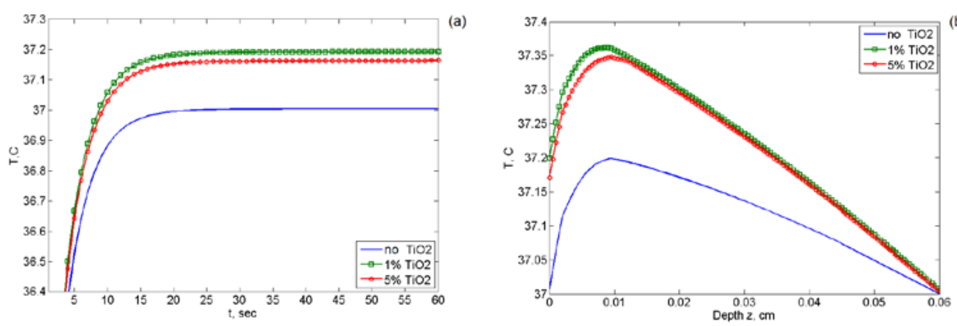

Fig. 3. Temperature dynamics on the skin surface (a) and in depth (b) in absence and presence of TiO_2 particles (diameter 100 nm) in stratum corneum. Weighted contribution of the three wavelengths: 310 nm – 5%, 514 nm – 50%, 800 nm – 45%. Cooling takes place due to convection (100 W/m^2K) and internal heat drainage (blood perfusion).

4. Discussion

In the absence of TiO_2 particles, the main contributors to the skin heat load are 310- and 514-nm light in stratum corneum and 514- and 800-nm light in epidermis (Fig. 2(a)). Due to deeper penetration of the 514- and 800-nm wavelengths in comparison to 310-nm light, they cause the main heat load to the skin. This is illustrated by the areas under the corresponding curves in Fig. 2. Administration of the particles results in multiple increase of absorption in the superficial part of the stratum corneum with particles (z = 0-3 μm); in the rest part of the

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layer (without particles) as well as in epidermis and dermis we observe almost the same level of the absorbed energy density (as without nanoparticles). The 514-nm light retains its main role in the contribution to the absorbed energy in stratum corneum (in the sublayer without particles) also in the presence of nanoparticles, while the 800-nm light plays only a minor role in stratum corneum and comparable role in epidermis (at the depth of 20 μm and deeper). The particles absorb strongly 310-nm light, thus screening the rest part of stratum corneum from this wavelength fraction. And substantially weaker absorption of the light with $\lambda = 514$ nm is compensated by its larger weight contribution (50%) to the resulting curve compared to that of $\lambda = 310$ nm (5%). On average, in presence of 5% (1 μm) + 1% (2 μm) of particles, the absorbed energy density in the stratum corneum is more than twice higher than in case of 1% of them.

Relative share of energy absorbed within the uppermost 3-μm-thick layer of the stratum corneum regarding the whole stratum corneum (20-μm-thick) in presence of 0%, 1% (in 3 μm) and 5% (in 1 μm) + 1% (in 2 μm) TiO_2 nanoparticles, can be calculated as a ratio of the area under the resulting curves (denoted as "Sup") in Fig. 2 for depths of (0-3 μm) and (0-20 μm). This results in gradual increase of the contribution of the uppermost 3-μm-thick layer from 15% (no TiO_2) to 30% (1% TiO_2 in 3 μm) to 40% (5% (in 1 μm) + 1% (in 2 μm)) to the heat load.

The administration of TiO_2 nanoparticles has almost no influence on absorbed energy distribution in epidermis and dermis and the temperature increase is only 0.1°C (Fig. 3(b)), due to weak interaction between the particles and 514- and 800-nm light, thus allowing for undisturbed penetration of these wavelengths below the stratum corneum.

Temperature dynamics is caused by the internal heat drainage (blood perfusion) and by at least one more drainage, convection, located on the skin surface (boundary condition 2). The latter represents skin cooling by heat transfer to the ambient medium (air). In this paper, convective heat transfer coefficient A is set to 100 W/m^2K [19,20] and the external temperature equals 20°C. Initial temperature of skin will have a gradient ranging from ~34°C (on the skin surface) to 37°C (deep in skin). The convection can be intensified or inhibited by application of different substances onto the skin surface. For instance, sweat/water evaporation can increase amount of energy transferred from skin to the environment.

5. Conclusion

In this paper, we consider the effect of TiO_2 nanoparticles (100 nm in diameter) embedded into the uppermost layer of skin on distribution of density of absorbed light and on temperature dynamics on skin surface under simulated sunlight irradiation. For simplicity, sunlight comprised three wavelengths: 310 nm (UV), 514 nm (visible) and 800 nm (IR), with correspondingly weighted contribution of 5%, 50% and 45%. This causes overestimation of the heat load due to exclusion of longer wavelengths from the consideration.

We have found that increasing amount of the absorbed radiation (15-30-40%) is accumulated in the 3-μm-thick superficial part of stratum corneum before and after administration of 1% (in 3 μm) and 5% (in 1 μm) + 1% (in 2 μm) TiO_2 nanoparticles. In case of both heat transfer sources (convection on the skin surface and blood perfusion inside the skin), the temperature increases by 0.2°C in presence of TiO_2 nanoparticles for the simulated sunlight, thus posing no heat overload to skin.

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